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Occurrence, characterisation and fate of (nano)particulate Ti and Ag in two Norwegian wastewater treatment plants

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1. Introduction

Owing to their widespread application in consumer products (clothing, cosmetics and personal care products), titanium (Ti) and silver (Ag) nanomaterials are increasingly released to sewer networks and wastewater treatment plants (WWTPs) from households and industries [1,2]. A number of attempts have been made to quantify and characterize single element fractions (i.e. particulate, colloidal and dissolved) in wastewater [2,3]. Furthermore, temporal trends (e.g., diurnal variations) in the occurrence of Ti and Ag in WWTP influents are largely unknown, and their elucidation could help understanding sources of discharge. While several studies have investigated the fate and removal of (nano)metals in pilot- and full-scale biological treatment plants [2–4], limited evidence exists for facilities employing only preliminary and primary treatment steps. These facilities, which typically exhibit reduced removal of conventional pollutants (organic matter, nutrients), are the most common in Norway. Evaluating the removal of (nano)metals in these facilities can thus be crucial in quantifying emissions to environmental compartments. The objectives of the current study were to: (i) assess diurnal and intra-day variations in the occurrence of Ti and Ag in the influent of two Norwegian WWTPs during a one-week sampling campaign; (ii) develop and evaluate a comprehensive method to characterize Ti and Ag in WWTP influents as (nano)particulate, colloidal and dissolved fractions; and (iii) quantify the removal of Ti and Ag in the two WWTPs, employing preliminary and primary treatment.

2. Materials and methods

A seven-day dry-weather sampling campaign was conducted at the two main WWTPs in Trondheim, Norway, Ladehammeren (LARA, capacity = 120,000 PE) and Høvringen (HØRA, capacity = 170,000 PE). Both WWTPs have significant industrial contribution (up to 50% of influent for LARA) and employ fine screening, sand and fat removal, chemically-aided flocculation, and sedimentation as treatment units. Effluents from the WWTPs are discharged to the Trondheim Fjord. Composite influent and effluent samples were collected by means of automatic samplers. Eight-hour flow-proportional samples (frequency=5 min) were collected to assess diurnal Ti and Ag loading variations in the influents. The 8-h intervals were selected to cover morning (M), evening (E) and night (N) discharges. Twenty-four-hour flow proportional and volume-proportional influent and effluent samples were further collected to assess Ti and Ag removal during wastewater treatment. Characterization of Ti and Ag in influent samples was carried out through size-based fractionation of untreated wastewater (initial sample volume = 85–100 mL). First, sequential filtration steps (2.7 µm and 0.7 µm pore size glass fibre filters, Whatman, USA) were used to separate the particulate fraction. Subsequent membrane ultrafiltration (3 kDa) of the 0.7 µm filtrate was performed to isolate the dissolved (ionic) fraction from the colloidal fraction. Ti and Ag were quantified in untreated samples, the 0.7 µm filtrate, and 3 kDa filtrate using inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

Figure 1a shows the diurnal profiles of total Ti and Ag concentrations in WWTP influents (from 8-h composite samples) over 7 days. Comparable Ti concentrations were quantified in LARA (41–195 µg L^{-1}) and HØRA (54–211 µg L^{-1}) influents, being significantly higher than Ag concentrations (<0.15–2.2 µg L^{-1}). Notably, rather different diurnal profiles were observed for the two elements. Ti concentrations followed typical diurnal trends of influent flow rate and pollutant concentrations in municipal WWTP influents (morning and/or evening peaks, night minima; as an example, see 8-h fractions of daily total flow in Figure 1a). A more irregular pattern was observed for Ag concentrations, possibly resulting from short-term release to sewers and WWTPs. This seems to indicate that Ti discharge followed typical trends of household discharges, whereas Ag emissions to WWTPs may be associated to one or few point sources (e.g., industries). Most of the influent Ti and Ag occurred in particulate form or was associated with influent solids (Figure 1b), in agreement with previous findings [2,5]. Approximately 5% of Ag was found to occur in colloidal or ionic form, while these two fractions were almost negligible for Ti (0.2%). A detailed characterization using transmission

electron microscopy and X-ray photoelectron spectroscopy, currently in progress, aims to identify Ti and Ag nanoparticles in each fraction (if present). Removal efficiencies of Ti and Ag in LARA and HØRA were calculated by comparing total effluent concentrations in 24-h influent and effluent samples (Figure 1c). Ti removal efficiency in HØRA was typically >80%, whereas significantly reduced elimination was observed in LARA (37.5%). Although these varying removal efficiencies are within previously observed ranges for preliminary and primary treatment [2], observed differences may be associated with the different removal of suspended solids in the two WWTPs. Conversely, comparable Ag removal efficiencies were observed in the two WWTPs (78.2% in LARA, 69.2% in HØRA).

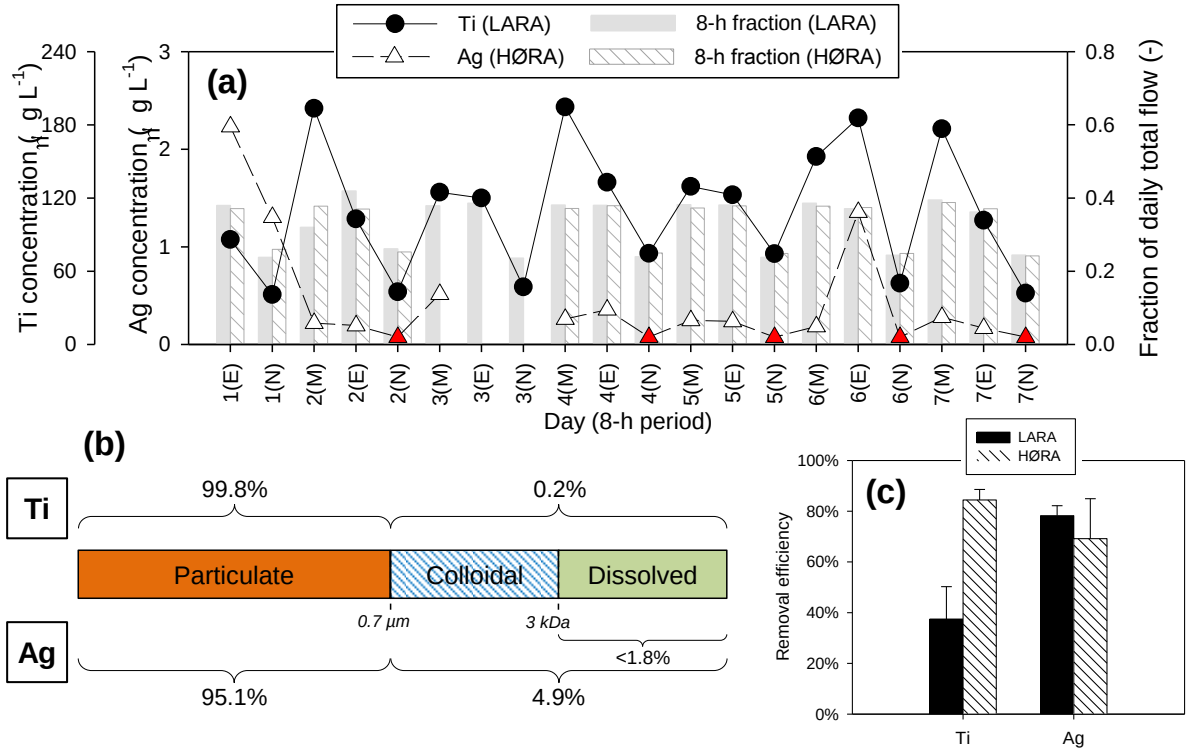

Figure 1. (a) Diurnal variations in the occurrence of total Ti and Ag in LARA and HØRA WWTP influents, respectively, during the seven-day sampling campaign. For Ag, red symbols denote concentrations below the limit of quantification (here shown as 0.5·LOQ). (b) Fractionation of Ti and Ag in WWTP influents, and % composition of each fraction (Ti: n=38; Ag: n=16). (c) Calculated removal efficiencies of Ti and Ag in LARA and HØRA (average and standard deviation, n=6)

4. Conclusions

A sampling campaign was conducted in two full-scale Norwegian WWTPs to quantify and characterise Ti and Ag in untreated influent wastewater and their removal along the treatment train. Significantly different concentrations and diurnal occurrence patterns were observed for Ti and Ag in the two WWTPs. Following the application of a comprehensive fractionation method, Ti and Ag were quantified mostly (> 90%) in particulate form (>0.7 µm). Removal efficiencies ≥ 70% were determined for both elements except for one WWTP, where Ti removal < 40% was observed. Ongoing research is currently focusing on verifying the occurrence of Ti and Ag in nanoparticulate form and at predicting dynamics in Ti and Ag occurrence in WWTP influents using influent generator algorithms.

5. References

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